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Novel Phosphaalkene-Based Late Transition Metal Complexes: Synthesis and Applications

Phosphaalkenes are emerging as a new class of phosphorus ligands endowed with specific electronic properties. Their unique donor—acceptor properties offer interesting perspectives in coordination chemistry and catalysis. Phosphaalkenes are accessible via a variety of synthetic routes but in the past decade, the phospha-Wittig reaction has appeared as the most promising pathway to afford phosphaalkenes. Phosphanylidenephosphoranes or phospha-Wittig reagents R—P(PR'3) are a powerful tool in synthetic inorganic chemistry and have found applications in the formation of phosphaalkenes using the so-called phospha-Wittig reaction, as well as valuable phosphinidene-transfer reagents.

Therefore, the main objective of this work was divided into two parts. First, we aimed to further study the potential of phosphanylidenephosphoranes as phosphinidine-transfer reagents to access bulky NHC phosphinidene adducts. In addition, the electron-rich dicoordinate phosphanylidene P-atom was utilized in reactions with nucleophiles and the activation of E-H bonds. The facile activation of E-H bonds gave straightforward access to species of interest for materials chemistry as well as to ligands for homogenous catalysis. Next, we attempted to exploit the reactivity of phospha-Wittig reagents toward carbonyl compounds to make a variety of phosphaalkene based ligands. As a part of this thesis, we targeted to synthesize a number of P,N-type phosphaalkene based Rh and Ir complexes to study their reactivity and application in homogenous catalysis. When preparing these complexes, special attention is required with respect to reaction conditions as otherwise, C-H bond activated phosphaindane based metal complexes are obtained. Theoretical investigations on the mechanism of such C-H bond activation were a part of this thesis.